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VAPOR PRESSURE OF AMMONIUM PERCHLORATE[1]

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Abstract

The equilibrium vapor pressure of ammonium perchlorate has been measured in the temperature range of 520-620°K by the transpiration method. The data indicate that ammonium perchlorate sublimes by the dissociation process $NH_4ClO_{4(s)} = NH_{3(g)} + HClO_{4(g)}$. The heat of dissociation has been found to be 58 ± 2 kcal/mole in the cited temperature range.

Introduction

During the past several years some efforts have been directed to elucidating the mechanism of the decomposition[2-7] and combustion[8,9] of ammonium perchlorate (AP). Bircumshaw and Newman[2] found that the decomposition of AP below $513^{\circ}K$ in vacuum left a residue after 20-30% of the salt had decomposed. The residue, however, was confirmed to be pure AP by analytical and X-ray methods. Friedman and Levy[10] in their preliminary study of the reaction between NH_3 and $HClO_4$ reported

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2. L. L. Bircumshaw and B. H. Newman, Proc. Roy. Soc. A227, 115 (1954); A227, 228 (1955).
3. L. L. Bircumshaw and T. R. Phillips, J. Chem. Soc. 1957, 4741.
4. A. K. Galwey and P. W. M. Jacobs, J. Chem. Soc. 1959, 837; 1960, 5031.
5. A. K. Galwey and P. W. M. Jacobs, Trans. Faraday Soc. 55, 1165 (1959); 56, 581 (1960).
6. A. K. Galwey and P. W. M. Jacobs, Proc. Roy. Soc. A254, 455 (1960).
7. P. W. M. Jacobs and A. R. Tariq Kureishy, Eighth Symposium (International) on Combustion, The Williams and Wilkins Company, Baltimore, Maryland, 1962, p. 672.
8. R. Friedman, R. G. Nugent, K. E. Rumbel, and A. S. Scurlock, Sixth Symposium (International) on Combustion, Reinhold Publishing Corporation, New York, 1957, p. 612.
9. J. B. Levy and R. Friedman, Eighth Symposium (International) on Combustion, The Williams and Wilkins Company, Baltimore, Maryland, 1962, p. 663.
10. R. Friedman and J. B. Levy, Final Technical Report AFOSR 2005, Atlantic Research Corporation, Alexandria, Virginia (1961).

that solid formation was observed in the mixing chamber under certain experimental conditions which gave a crude measure of the vapor pressure of AP. This observation suggests that a dissociative process is involved in the sublimation of AP. It is apparent that the vapor pressure of AP represents an important parameter in the analysis of the combustion mechanism of solid propellants based on this oxidizer.

Apparatus and Procedure

The reagent grade AP from Matheson, Coleman and Bell Company was fractionated mechanically into two particle size ranges, 43-61 μ and > 61 μ; the material was not subjected to any purification.

In a typical experiment a weighed sample of AP was placed in a glass-fritted cell (Fig. 1) and brought to the desired temperature by immersing the cell in a bath of molten salt.[11] The temperature of the molten bath was carefully regulated and measured with a glass-sheathed iron-constantan thermocouple. The decomposition and dissociation products of AP were carried away in a helium gas stream passing in an upward direction through the glass frit and the powdered sample. The volumetric flow rate of helium was determined by suitable calibrated flowmeters. All experimental measurements were carried out on that portion of AP which remains after decomposition of 20 to 30% of the original sample.[2]

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[11] J. A. Beattie, Rev. Sci. Instr. 2, 458 (1931).

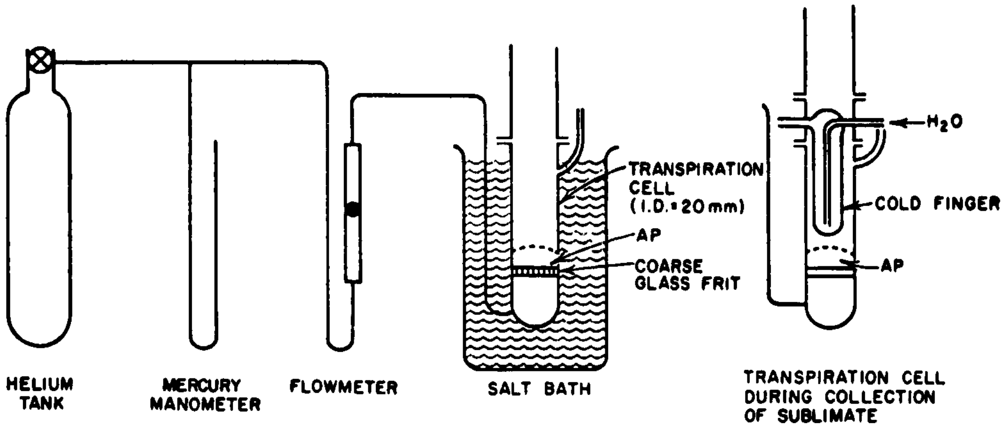
TRANSPIRATION CELL (I.D.=20 mm)
AP
COARSE GLASS FRIT
H_2O
COLD FINGER
AP
HELIUM TANK
MERCURY MANOMETER
FLOWMETER
SALT BATH
TRANSPIRATION CELL DURING COLLECTION OF SUBLIMATE

FIG. 1 SCHEMATIC DIAGRAM OF APPARATUS

Before the vapor pressure measurement, the sample was heated for approximately an hour. During the initial stage of decomposition a rapid exothermic reaction occurs which may elevate the temperature of the powder bed as much as 100°K above the bath temperature with the evolution of brownish-yellow vapors. The residual material was a porous, amorphous solid, which crumbled easily. At this time a water-cooled cold finger was quickly placed in position in the transpiration cell (Fig. 1). The distance between the cold finger and the sample was about 2 cm in most experiments; in some cases it was increased to 4 cm. The temperature of the water in the cold finger was maintained at approximately 340 ± 10°K to prevent the condensation of H_2O. After a suitable reaction time, the finger was removed carefully and the white sublimate washed into a flask with about 50 ml of distilled water. The solution was analyzed primarily for NH_4^+,[12] ClO_4^- [13] and Cl^- [14] in some cases. The vapor pressure of AP may be readily deduced from the flow rate of helium and the quantity of AP deposited on the finger.

Results and Discussions

In a number of runs the following major parameters were varied: (1) flow rate of helium gas, (2) reaction temperature, (3) initial mass of AP, (4) initial particle size, and (5) partial pressure of NH_3 added to carrier gas. As shown in Table I the sublimates analyzed were found to contain equimolar quantities of NH_4^+ and ClO_4^- ; therefore, the results may be interpreted in terms of an equilibrium dissociation of NH_4ClO_4 :

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[12] F. D. Snell and C. T. Snell, Colorimetric Methods of Analysis, 3rd. ed. Vol. II, D. van Nostrand Company, Inc., New York, 1949, p. 815.

[13] E. A. Burns and R. F. Muraca, Anal. Chem. 32, 1316 (1960).

[14] D. M. Coulson and L. A. Cavanagh, Anal. Chem. 32, 1245 (1960).

$$NH_4ClO_{4(s)} = NH_{3(g)} + HClO_{4(g)} \qquad (1)$$

Since equivalent amounts of NH_3 and $HClO_4$ are produced, the dissociation pressure P_d is equal to the sum of P_{NH_3} and P_{HClO_4} provided there is no excess of either gas initially. The calculated vapor pressures based on the analyses of NH_4^+ and ClO_4^- are in satisfactory agreement. The small variations observed are within the precision of the analytical techniques estimated to be ± 10% for NH_4^+ and ClO_4^- . Based on these data the dissociation pressures are plotted against the reciprocal of the absolute temperature as shown in Fig. 2. The resulting line may be expressed by the equation:

$$\log_{10} P\ (\text{mm}) = -\frac{6283.7}{T} + 10.56 \qquad (2)$$

In our experiments the flow rate of the carrier gas was selected sufficiently high so that the mass transfer from the powder to the cold finger was not diffusion-limited. Yet the flow velocity was kept low enough to eliminate mechanical carry-over of particulate matter. The absence of mechanical transport of powdered AP particles onto the cold finger could be demonstrated by: (1) the agreement observed in experimental measurements of vapor pressures in which the flow velocity was increased by a factor of two, and (2) the nonappearance of a deposit at

Table I

EXPERIMENTAL CONDITIONS AND DATA ON DISSOCIATION VAPOR PRESSURE MEASUREMENTS

RUNS	BATH TEMP. (°K)	INITIAL MASS OF AP (gm)	FLOW RATE (cc/min)	COLLECTION TIME (min)	TOTAL MOLES IN SUBLIMATE (mole x 10^3)			VAPOR PRESSURE (mm) BASED ON		REMARKS*
					NH_4^+	ClO_4	Cl	NH_4^+	ClO_4^-	
1	523	1.00	152	90	0.012	--	--	0.032	--	43-61 μ
2	523	2.00	152	135	0.016	--	--	0.028	--	43-61 μ
3	525	2.00	152	105	0.014	--	--	0.032	--	
4	525	6.00	152	90	0.013	--	0.0017	0.035	--	
5	528	2.00	152	105	0.021	0.024	0.0010	0.049	0.057	AP sample heated for more than 4 hours before collection
6	537	2.00	152	85	0.024	--	--	0.070	--	
7	538	2.00	152	70	0.029	--	--	0.079	--	
8	547	6.00	152	120	0.047	--	--	0.098	--	
9	548	2.00	152	60	0.034	0.035	--	0.14	0.14	
10	551	1.00	293	100	0.113	--	--	0.14		43-61 μ
11	551	1.00	152	90	0.053	--	--	0.14	--	43-61 μ
12	551	2.00	152	60	0.038	--	--	0.15	--	
13	561	2.00	152	60	0.047	--	--	0.20	--	
14	561	2.00	152	60	0.057	--	--	0.23	--	Distance between powder bed and cold finger is 4 cm
15	561	2.00	293	63	0.097	--	--	0.19	--	
16	561	6.00	152	60	0.051	--	--	0.21	--	
17	562	2.00	293	60	0.0045	--	0.0025	--	--	20 cc/min NH_3 added
18	577	2.00	152	60	0.098	--	--	0.40	--	
19	575	2.00	293	60	0.19	0.19	pos	0.41	0.40	
20	573	2.00	152	60	0.090	0.085	--	0.37	0.32	AP sample heated for more than 4 hours before collection
21	588	2.00	152	63	0.19	0.16	pos	0.74	0.64	
22	588	2.00	152	60	0.20	0.17	pos	0.81	0.70	
23	600	2.00	152	60	0.027	nil	0.027	--	--	20 cc/min NH_3 added
24	600	2.00	152	30	0.15	0.15	--	1.26	1.23	Distance between powder bed and cold finger is 4 cm
25	602	2.00	152	30	0.15	0.13	0.0087	1.19	1.09	
26	615	2.00	152	30	0.28	--	--	2.29	--	
27	616	2.00	152	30	0.27	0.28	0.0018	2.24	2.26	

* Initial particle size > 61 μ, and, distance between powder bed and cold finger 2 cm, except where noted.

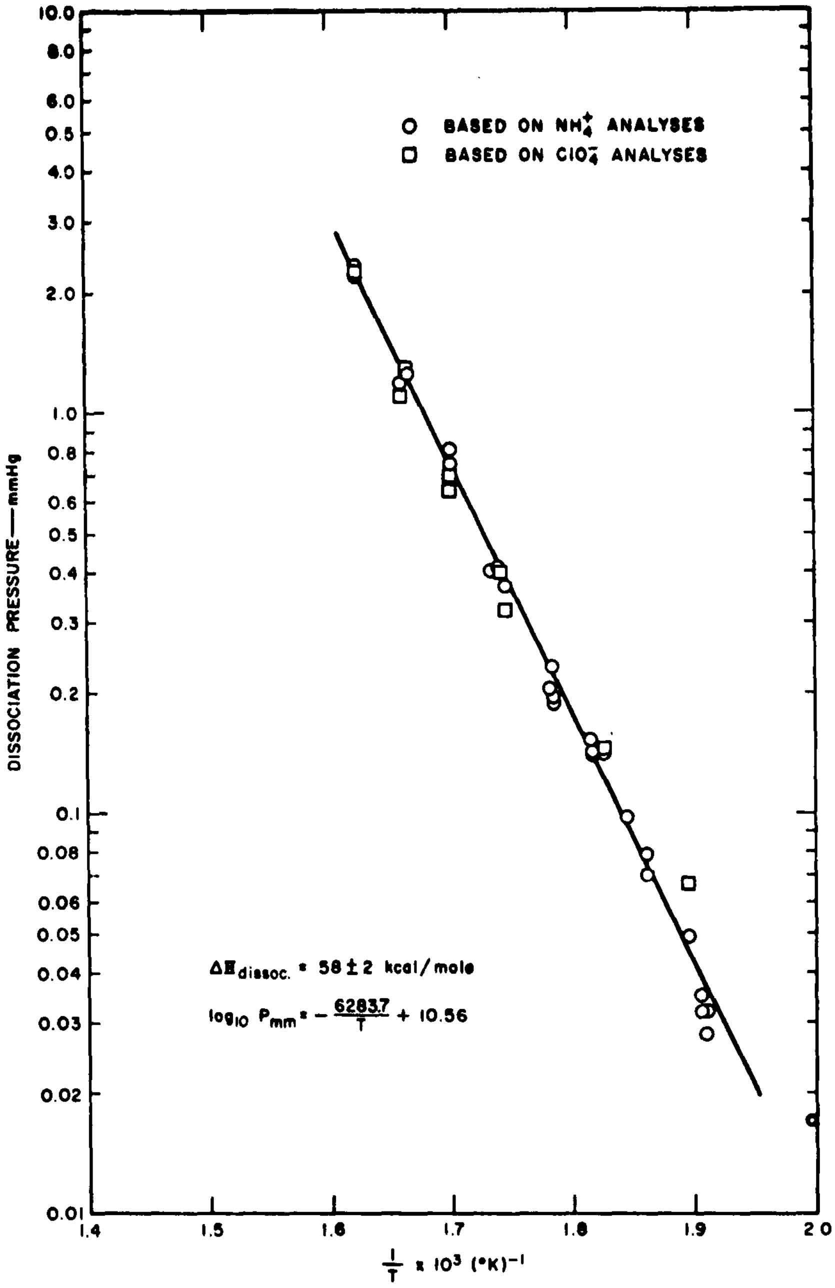

FIG. 2 DISSOCIATION PRESSURE OF AMMONIUM PERCHLORATE

temperatures at which dissociative sublimation is negligibly small. Under these experimental conditions there is no evidence of any serious cooling of the powder, since the results obtained are comparable within the experimental precision when the finger is placed 2 cm or 4 cm from the bed (Table I, runs 14 and 24). In addition, it can be shown that the decomposition of $HClO_4$ is negligibly small in the temperature range studied from the rate constant for the decomposition of gaseous perchloric acid reported by Levy.[15]

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[15] J. B. Levy, AFOSR TN 1555, Atlantic Research Corporation, Alexandria, Virginia (1961).

To test the saturation of the carrier gas by the dissociation products, the flow rate of helium gas was varied by a factor of two and the initial mass of the sample by a factor of six. A decrease in the flow rate of helium and an increase in the initial mass of the sample will tend to favor saturation of carrier gas since the residence time of the products is increased. Under most favorable conditions (helium flow of 152 cc/min and a 6-gram sample) the results obtained were comparable to runs made under most unfavorable conditions (low mass + high flow).

Experimentally the vapor pressure measurements were limited to a temperature range from 510°K to 620°K. At lower temperatures the quantity of sublimate collected within a reasonable length of time was too small for analysis; at temperatures above 620°K the decomposition of the perchloric acid can no longer be neglected.

During the determination of the vapor pressure of AP, it has been observed that dissociation (reaction 1) and thermal decomposition occur simultaneously. After the sample was heated for an hour at 513°K the pressure of the decomposition products calculated from the composition of the gas mixture as determined by thermal conductivity measurements was found to be roughly three times greater than the dissociation pressure. Experiments at 498°K and at 573°K in which the sample was heated for more than four hours before starting collection of dissociation products gave vapor pressure data in good agreement with those runs in which the sample was heated for a much shorter time (Table I, runs 5 and 20). On the basis of these results it may be assumed that the thermal decomposition reaction does not affect the dissociative sublimation.

As indicated in Table I, the sublimates were found to contain, besides NH_4^+ and ClO_4^-, small amounts of Cl^- (2-3 mole %). In the sublimates collected from experiments in which 20 cc/min of NH_3 were introduced to the carrier gas, equimolar amounts of NH_4^+ and Cl^- were found to be present; however, only traces of ClO_4^- were detected (see runs 17 and 23). A simple calculation shows that when NH_3 is added the pressure of $HClO_4$ is suppressed to nearly zero. From these results it is reasonable to assume (1) that the chloride ion is most likely present as NH_4Cl arising from the interaction of Cl_2 (thermal decomposition product) with NH_3 :

$$8\ NH_3 + 3\ Cl_2 = 6\ NH_4Cl + N_2 \qquad (3)$$

and (2) that the AP sublimes by the dissociation process (reaction 1).

As indicated by reaction 3, for each mole of NH_3 that reacts with Cl_2, $\frac{3}{4}$ of a mole is recovered as NH_4^+.

Since the chloride analyses were made in only a few runs and the precision of the analysis of Cl^- was probably ± 10%, no attempts were made to compensate for this small loss of NH_4^+. Due to this small loss the error in the calculated vapor pressure based on the NH_4^+ is estimated to be smaller than the analytical errors. On the other hand, the loss of NH_3 by reaction 3 reduces the amount of $HClO_4$ on the cold finger. Consequently, the error in the calculated vapor pressure based on the ClO_4^- analysis is somewhat larger.

The entropies of sublimation with dissociation at pressure of 10 mm Hg were calculated for NH_4Cl,[16] NH_4NO_3,[17] and NH_4ClO_4 and are listed in Table II. The entropy of AP is consistent with the other ammonium

Table II

ENTROPY OF DISSOCIATION

Compounds	(ΔH dissoc.) kcal/mole	Temp. at which Dissoc. Press. = 10 mm (°K)	ΔS at cited temp. (cal/deg mole)
$NH_4NO_{3(\ell)}$	39.8	485	~ 82
$NH_4Cl_{(s)}$	39.4	483	~ 83
$NH_4ClO_{4(s)}$	58	657(a)	~ 88

a. Based on extrapolation to 10 mm.

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[16] W. H. Rodebush and J. C. Michalek, J. Am. Chem. Soc. 51, 748 (1929).

[17] G. Feick, J. Am. Chem. Soc. 76, 5858 (1954).

compounds which further suggests the equilibrium dissociation of AP (reaction 1) rather than sublimation of a NH_4ClO_4 molecule as an entity. The latter fact is further substantiated by the pronounced suppression of sublimation by ammonia gas in the carrier stream as observed in our experiments.

Since the thermodynamic data of heats of formation are not precisely known, it is not possible to check accurately the experimental value of heat of dissociation with a value calculated from reaction 1. The room temperature value, however, can be estimated by using the following data:[18]

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[18] National Bureau of Standards Report No. 7437, "Preliminary Report on the Thermodynamic Properties of Selected Light-Elements and Some Related Compounds," Jan. 1962.

Substance	$(\Delta H_f^0)_{298}$ (kcal/mole)
$NH_4ClO_{4(s)}$	- 70.7
$NH_{3(g)}$	- 11.0
$HClO_{4(\ell)}$	- 9.8

If it is assumed that the heat of evaporation of $HClO_{4(\ell)}$ is the same as that for $HNO_{3(\ell)}$ (9.4 kcal/mole), then $(\Delta H_f^0)_{298}$ for $HClO_{4(g)}$ becomes -0.4 kcal/mole. On the basis of these values, the heat of dissociation of $NH_4ClO_{4(s)}$ is calculated to be 59.3 kcal/mole, a value only slightly different from that obtained experimentally at higher temperatures.

Acknowledgment

The authors are indebted to Mr. Oliver Smith and Miss Elizabeth McCarthy for the chemical analyses.